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Singlet oxygen oxidation of selenides to selenoxides

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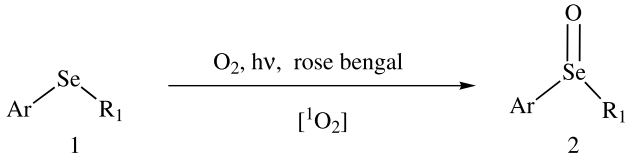
Abstract—The presence of water and a carbonate proved to be highly beneficial for singlet oxygen oxidation of selenides to selenoxides.

Several years ago, we disclosed[1] that singlet oxygen, produced by shining light on molecular oxygen and trace amount of rose bengal, is able to efficiently oxidize in methanol, selenides to selenoxides (Scheme 1).[1]

Since that time, this reaction was successfully used (i) by Abadjoglou[2] for the reoxidation of Os(VI) to Os(VIII) implied in the dihydroxylation of olefins and (ii) by us[3a] for its asymmetric version (SeAD reaction, Scheme 2). The SeAD reaction is very close to the Sharpless AD reaction[4] but uses oxygen in place of potassium ferricyanate as the co-oxidant (Scheme 2).[3a]

It is not clear whether the selenoxide, or a putative peroxoselenide intermediate, is the effective oxidant. However, in a parallel work, which involved a stoichiometric amount of selenoxides, we were effectively able to prove that selenoxides are valuable co-oxidants in the SeOAD reaction.[3b]



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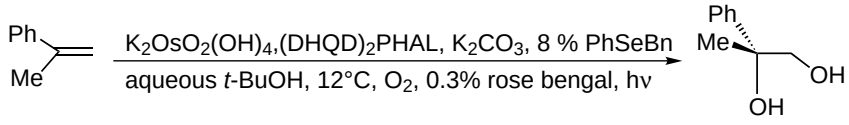
Scheme 1. Oxidation of selenides to selenoxides using singlet oxygen.

As an extension of this work, we also disclosed[3b] that the rate of the SeOAD reaction was highly dependent upon the nature of the selenoxide. Dialkyl selenoxides are less efficient than alkyl aryl selenoxides[3b,c] and the presence of an electron-withdrawing group on the aromatic ring proved to be highly beneficial.

It was obvious that these findings would have an important impact on the SeAD reaction. In this case, the problem was expected to be more complex due to the fact that those aryl selenides which possess an electron-withdrawing group on their aromatic ring are those which are usually the most difficult to oxidize. Consequently it was important to know which of the two steps (oxidation of the selenide or reduction of the selenoxide) is the rate-limiting one.

We decided to get a more detailed picture of the reactivity of singlet oxygen toward selenides and planned to extend this reaction to the whole series of selenoxides used in the previous work[3b] and to carry out kinetic comparative studies.

We first performed the reaction on benzyl phenyl selenide (10^{-2} M, oxygen, 10^{-4} M rose bengal, methanol,



Scheme 2. Asymmetric dihydroxylation of α-methyl styrene (SeAD reaction) using selenides and singlet oxygen.[3a]

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Table 1. Reaction of selenides **1** with singlet oxygen under different experimental conditions according to Scheme 1

	Conditions			I	II	III
	Ar	R_1	T[a]	**2**/**1** MeOH	**2**/**1**[b1] + H_2O	**2**/**1**[b2] + H_2O + K_2CO_3
a	Ph	$PhCH_2$	4	12/88	67/33	99/1
b			16	50/50	98/2	
c	*p*-NO_2-Ph	$PhCH_2$	4	0/100	0/100	4/96
d	*p*-MeO-Ph	$PhCH_2$	4	21/79	84/16	99/1
e	Ph	Me	4	43/57	99/1	100/0
f	Ph	Ph	4	0/100	3/97	44/56
g			16	0/100	6/94	95/5

[a] T refers to the reaction time quoted in hours.
[b] These reactions have been carried out in 0.01 M solution (1) in MeOH/H_2O (6/3) or (2) in MeOH/H_2O (6/3) in the presence of 0.5 M equiv. of K_2CO_3.

light,[†] 20°C)[1] under conditions closely related to those we previously used and were surprised to get after 4 h reaction only a small amount of the corresponding selenoxide (**2a**/**1a** 12/88, Scheme 1, Table 1 entry Ia) whereas in our original paper we reported a much better yield of benzyl phenyl selenoxide after a much shorter reaction time (70%, 2.5 h).[1] It was moreover not an isolated case as, except for methyl phenyl selenide (Table 1, entry Ie) which proved to be a little more prone to oxidation, all other aryl selenides proved to be reluctant to react (Table 1, entry I). All the modifications we tried (lamp,[‡,§] quality of oxygen, careful drying and distillation of methanol) unfortunately did not improve the results.

We finally planned to carry out this reaction in different solvents.

Little choice remains since several non-polar solvents such as toluene or methylene dichloride do not dissolve rose bengal enough to allow the reaction. We tried unsuccessfully to perform the reaction (i) in other alcoholic solvents such as ethanol, *i*-propanol and *t*-butanol or (ii) in acetonitrile or in acetone (Table 2, entry I).

We, however, surprisingly found[§] that benzyl phenyl selenoxide is produced at a faster rate if the reaction is carried out in wet methanol (Table 1, entry IIa, compare to entry Ia). A larger amount of water increases substantially the reaction rate up to a certain point (MeOH/H_2O [**2a**/**1a**]: 100/0 [12/88]; 90/10 [15/85]; 80/20 [33/67]; 70/30 [55/45]; 66/33 [67/33]) from which a sharp decrease occurs due to the insolubility of the selenide in the medium (MeOH/H_2O [**2a**/**1a**]: 60/40 [60/40]; 50/50 [37/63]). We have then successfully performed the synthesis of a few other selenoxides by performing the reaction in methanol/water (6/3) (Table 1, entry II compare to entry I). We were unable to oxidize *p*-nitrobenzyl phenyl selenide but we have produced, although in small amount (6%), diphenyl selenoxide from diphenyl selenide (Table 1, entry g). It is interesting to recall that it has been firmly established that singlet oxygen is unable to oxidize the analogous diphenyl sulfide.[5,6]

It is not obvious to rationalize the role of water in this reaction since it was believed, until recently, to be a singlet oxygen scavenger.[6] Nevertheless a very recent paper stresses the "unusual regiochemical dependence" of the singlet oxygen ene-reaction involving tiglic acid and related esters towards the polarity of the solvent.[7] Interestingly, these reactions have been carried out in methanol and in methanol/water (60/40) and differences have been noticed.[7]

In relation to very recent findings,[8] singlet oxygen could also have produced hydrogen peroxide which is an efficient oxidant of selenides to selenoxides. However the inaptitude of the newly developed method to oxidize

Table 2. Reaction of benzyl phenyl selenide **1a** with singlet oxygen in different solvents and with different additives according to Scheme 1

	Conditions[a]	I	II	III
	Solvent	**2**/**1**[b1] Neat	**2**/**1**[b2] + H_2O	**2**/**1**[b3] + H_2O + K_2CO_3
a	MeOH	12/88	67/33	99/1
b	EtOH	0/100	10/90	97/3
c	*i*-PrOH	0/100	0/100	65/35
d	*t*-BuOH	0/100	0/100	39/61
e	MeCN	0/100	0/100	61/39
f	Me_2C=O	0/100	0/100	30/70

[a] In all cases, reaction time is 4 h.
[b] These reactions have been carried out in 0.01 M solution in (1) the solvent (2) an aqueous solution (solvent/H_2O: 6/3) or (3) an aqueous solution (solvent/H_2O: 6/3) in the presence of 0.5 M equiv. of K_2CO_3.

[†] In our original work we used a lamp which is no longer available.[1]
[‡] We have performed these reactions using (i) two halogen spots (Osram Haloline 230 V, 500 W emitting mainly in the visible region and providing each one 9500 lumens, (ii) four economic cold light lamps (Osram Delux EL, 230 V, 23 W) providing 1580 lumens each, and (iii) two sodium lamps (Philips SDW-T, 230 V, 50 W providing 2300 lumens each. All three sources provide very closely related results on benzyl phenyl selenide.
[§] For convenience the Philips SDW-T lamp has been mostly used in this work.

Table 3. Reaction of benzyl phenyl selenide with singlet oxygen in different solvents and with different additives

	Time (h)	PhSMe ratio	PhS(O)Me ratio	$PhS(O)_2Me$ ratio
Anhydrous methanol	4	55	39	6
	16	04	74	22
Aqueous methanol	4	00	89	11
Aqueous methanol + K_2CO_3	4	02	90	8

p-nitro-phenyl benzyl selenide sheds some doubt on this hypothesis since we have independently found that *p*-nitro-phenyl benzyl selenoxide is effectively generated on reaction with hydrogen peroxide under closely related conditions.[9]

Singlet oxygen could also participate in the reaction by stabilizing or trapping one of the multiple postulated intermediates which finally leads to the selenoxide. We do not yet have tangible arguments in favor of one of the hypotheses disclosed above or any other alternative explanation. Anyhow, the reaction is slower when performed in deuterated methanol (MeOD)[¶] instead of methanol, attesting thus the important role of the solvent.

Even more interesting is the fact that the effect we have just reported is substantially enhanced by carrying out the reaction in aqueous methanolic solution containing potassium carbonate (Table 1, entry III). The best results have been observed when the reaction is performed with a 0.5 M equiv. of this inorganic compound. Two extreme cases merit discussion: on the one hand these conditions still do not allow the oxidation of *p*-nitro-phenyl benzyl selenide (Table 1, entry IIIc), and on the other hand they permit the efficient oxidation of diphenyl selenide to diphenyl selenoxide (Table 1, entry IIIg).

The observations reported apply to a wide range of alcoholic solvents for which increasing reactivity is found if the reaction is carried out in the presence of water or aqueous potassium carbonate solution (Table 2, entries II, III). These results express the trends and do not reflect the best conditions for selenoxide synthesis. For example, in *t*-butanol, benzyl phenyl selenide is more efficiently oxidized if the reaction is performed with 3 instead of 0.5 M equiv. of potassium carbonate (Table 3).

The real role of potassium carbonate in these reactions has not yet been comprehended. Evidence that it does not play the role of a base comes from the observation that it favors the oxidation of diphenyl selenide which obviously does not contain acidic hydrogens. We are actively working to identify the role of water and potassium carbonate in these reactions.

Interestingly, preliminary results tend to show that sulfides exhibit a closely related behavior although both the sulfoxides and the sulfones are simultaneously produced whatever conditions are used. For example, photoxidation of methyl phenyl sulfide in methanol/water produces the corresponding sulfoxides and sulfones more efficiently than in methanol alone (Table 3). Photoxidation of diphenyl sulfide however still remains a problem.[6]

[¶] Only a trace amount of benzyl phenyl selenoxide has been once obtained instead of a 12% yield when the reaction is carried for 4 h in MeOD in place of MeOH.

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